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3 NANOSIZE PARTICLE COATINGS MADE BY THERMALLY SPRAYING SOLUTION

4 PRECURSOR FEEDSTOCKS

5
6 Background of the Invention7 **1. Field of the Invention**

8 This invention relates to a thermal spray process which uses solution precursors as a
9 feedstock.

10 **2. Description of the Related Art**

11 Coatings are commonly used to provide desirable surface properties of the underlying bulk
12 substrates. Examples of protective coatings include wear-resistant, corrosion-resistant and thermal
13 barrier coatings. In many applications, multiple properties of the coatings are often desirable.
14 However, it is not always possible to have a single material (single phase material, alloy or
15 composite) that has all the required properties. In such a case, multiple materials with different
16 properties can be used in the form of multilayers.

17 Conventional coatings, including multilayered coatings, are made of coarse-grained materials
18 with grain sizes which are greater than several microns. These coatings can be prepared by solution
19 chemistry, physical or chemical vapor deposition or thermal spraying. For deposition methods that
20 do not involve solution based chemistry, physical vapor methods such as sputtering and beam

Inventor's Name: Gan-Moog Chow, Lynn K. Kurihara, T. Danny Xiao, Peter R. Strutt,
Christopher W. Strock and Raymond A. Zatorski

1 induced evaporation are commonly used. The vapor of the materials (as atoms or clusters) condense
2 on the substrate to form coatings. The chemical vapor approach generally involves pyrolysis of
3 chemical precursors at the substrate to form desirable reaction product coatings. Vapor techniques
4 are generally suitable for preparing thick films or thin coatings due to the low rate of deposition.

5 An alternative approach to fabrication of thick coatings is thermal spraying. In thermal
6 spraying powders are generally used as the feedstock and fed into a flame aimed at the surface of
7 substrates. The powders are propelled in the gas flow and are fused to form coatings on the substrate.

8 Thermal spraying includes plasma methods in the ambient atmosphere or vacuum, high velocity
9 oxyfuel spraying or high velocity impact fusion spraying. In all cases, the feedstock are often very
10 coarse agglomerates of powders. The agglomerate size is typically in the tens of microns. The
11 powder agglomerates often form splat microstructures, which are pancake-like structures in the
12 thermally sprayed coatings.

13 Although thermal spraying is a viable approach to preparing thick coatings, the use of the
14 powder agglomerate feedstock has limitations and problems. First, the sprayable powders often
15 require reprocessing from the parent powders by controlled agglomeration, which adds more cost
16 to the production and often introduces impurities if surface-active precursors are used as binders.
17 Second, the splat boundaries in the as-sprayed coatings are often the initiation sites for flaw
18 propagation that consequently lead to mechanical failure of the coatings. Third, the as-formed splat
19 microstructures present a limitation on the scale of chemical homogeneity and mixing of multiphasic
20 materials when desired because the splat is at least greater than several microns thick, due to the

Inventor's Name: Gan-Moog Chow, Lynn K. Kurihara, T. Danny Xiao, Peter R. Strutt,
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1 flattening of the molten particles on impact. From commercial experience, sprayable powders need
2 to be of a certain size such as about 30 microns or larger for efficient deposition. As a result,
3 reconstitution of nanoscale powder to 30 micron-sized agglomerates is often required. Unfortunately,
4 these larger diameter agglomerates produce longer splat microstructures in the coating. These large
5 splat particles become a serious problem when multifunctional applications require multilayered,
6 hybrid coatings with fine, continuous interfaces, since the length scale of an interface is limited by
7 the splat microstructure.

8 To solve this fine gradient coating problem, we proposed to use liquid solutions wherein the
9 composition of the solution is varied as the coating is applied. Although it has been known to use
10 a liquid feedstock in thermal spraying, such disclosures do not relate to the production of
11 nanostructure coatings and the multilayer and gradient coatings of the present invention.

12 U.S. Patent No. 5,032,568 to Lau *et al* uses an atomized aqueous solution containing at least
13 3 metal salts precursors into an inductively coupled ultra high temperature plasma for coating. There
14 is no discussion of forming nanostrucure coatings nor of how to provide multilayer and gradient
15 coatings on such a small scale.

16 U.S. Patent No. 4,982,067 to Marantz *et al* relates to an apparatus to eliminate the long-
17 standing problems with radial feed plasma spray apparatus by designing a true axial feed in a plasma
18 spray system. While most of this disclosure is to using particles as the feed, at column 5, lines 51-55,
19 the patent states that "alternatively, the feedstock may be in liquid form, such as a solution, a slurry
20 or a sol-gel fluid, such that the liquid carrier will be vaporized or reacted off, leaving a solid material

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1 to be deposited." Again, there is no discussion of forming nanostructure coatings nor of how to
2 provide multilayer and gradient coatings on this small scale. In addition this patent essentially deals
3 with the deposition of solid particles that are formed by conversion of the droplets to solid particles
4 in flight before impacting the substrate.

5 U.S. 5,413,821 to Ellis *et al* relates to an inductively coupled plasma to thermally decompose
6 a chromium bearing organometallic compound. Column 2, lines 19-22, states that the organometallic
7 compound can be introduced to the plasma as a vapor or a solid. However, in Example 4 the tetra-
8 methylchromium is cryogenically cooled to the liquid state for application to the plasma coating
9 device. The organometallic liquid was introduced into the plasma by bubbling through a carrier gas
10 or in the form of solid powder entrained in the carrier gas. The former may actually exist in the form
11 of chemical vapor. Again, there is no discussion of forming nanostructure coatings nor of how to
12 provide multilayer and gradient coatings on this small scale.

13 U.S. 5,609,921 to Gitzhofer *et al* discloses a suspension plasma spray where a suspension
14 of particles of the material to be deposited is in a liquid or semi-liquid carrier substance. An
15 inductively coupled radio-frequency plasma torch is used. The preformed particles are suspended
16 in a liquid carrier. Vaporization of the liquid carrier in the plasma leads to the agglomeration of the
17 particles. The particles become molten and impact the substrate. Suspension of small particles in a
18 liquid and its subsequent spraying into the plasma flame may lead to an additional problem. If the
19 particles are dispersed and are very fine (such as less than 100 nm), they may not have enough
20 momentum to penetrate into the plasma flame and be carried by the plasma flame to the substrate.

Inventor's Name: Gan-Moog Chow, Lynn K. Kurihara, T. Danny Xiao, Peter R. Strutt,
Christopher W. Strock and Raymond A. Zatorski

1 Again, there is no discussion of forming nanostructure coatings nor of how to provide multilayer and
2 gradient coatings on this small scale.

3

4 **Summary of the Invention**

5 It is an object of this invention to use of solution precursors as feedstock in thermal spraying
6 of ceramic, metallic, organic and hybrid (a combination of various classes of materials) coatings in
7 a potentially competitive, single step fabrication process for coatings.

8 It is a further object of this invention to provide a thermal spray process which eliminates the
9 need to synthesize powders and reprocess these powders for spraying.

10 It is a further object of this invention to utilize the chemical conversion of droplets in a
11 thermal spray process to form desirable reaction products as coatings on substrates in a single step
12 synthesis process.

13 It is a further object of this invention to provide a thermal spray process in which solution
14 feedstocks are employed for better homogeneity and mixing of multiphasic materials.

15 It is a further object of this invention to reduce costs for preparing coatings of high melting
16 temperature materials by replacing the melting of the powder required in conventional thermal spray
17 of powder feedstock with the lower temperature solidification of thermally sprayed droplets at the
18 substrate.

19 It is a further object of this invention to utilize the molecular design of solution precursors
20 for desirable reaction products in a thermal spray process.

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1 It is a further object of this invention to utilize an external energy source simultaneously
2 during the thermal spraying to affect the molecular design, structure, microstructure and interfaces
3 of the coating.

4 It is a further object of this invention to utilize a post deposition application of an external
5 energy source to further affect the molecular design, microstructure and interfaces of the coating.

6 It is a further object of this invention to employ a thermal spray process with a solution
7 feedstock in which the droplet size is varied.

8 It is a further object of this invention when using a thermal spray process with a solution
9 feedstock to further reduce droplet size by placing a fine screen mesh between the spray nozzle and
10 the substrate.

11 It is a further object of this invention when using a thermal spray process with a solution
12 feedstock to control the residence time, the in-flight temperature of droplet, and the working distance
13 to the substrate to control the structure and the microstructure of the deposited coatings.

14 It is a further object of this invention to employ a thermal spray process in which
15 fine droplets are allowed to solidify before reaching the substrate by controlling the in-flight
16 temperature so that the resulting splat will have a smaller dimension compared to that obtained by
17 using a powder feedstock.

18 It is a further object of this invention to employ a thermal spray process in which
19 droplets are allowed to reach the substrate in the liquid state so that solidification of droplets at the
20 substrate will also lead to finer splat microstructure and better chemical mixing when more than a

1 single phase of materials are sprayed.

2 It is a further object of this invention to employ a thermal spray process that is
3 suitable for producing multilayered materials that require fine scale grading, both compositionally
4 and microstructurally, and particularly for nanostructured graded materials.

5 It is a further object of this invention to employ a thermal spray process which permits the
6 integration of layers by gradually graded interfaces rather than abrupt interfaces so as to permit the
7 compatibility of hybrid multilayered materials, i.e. ceramics-ceramics; metal-ceramics; metal-metal,
8 organic-inorganic; and in any combination.

9 It is a further object of this invention to employ a thermal spray process which permits
10 microstructural, structural and chemical grading with continuous interfaces at a fine scale.

11 It is a further object of this invention to employ a thermal spray process in which
12 the process can be adapted to contain nanostructured pre-formed particles in solution so that the
13 solution provides the percolating matrix whereas the powders provide the major constituents of the
14 coating layers.

15 These and further objects of the invention will become apparent as the description of the
16 invention proceeds.

17 It has now been found that thin films or coatings can be made of nanostructured particles
18 which have a particle size less than 100 nm (i.e. 0.1 micron) by thermally spraying a solution of a
19 liquid coating precursor feedstock onto a substrate to form the film or coating. The resulting thin
20 film or coating has a thickness of about 100 nanometers or larger. By using thermal spraying with

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1 different precursor feedstock solutions, coatings can be made with more than one layer. Within a
2 given layer, by varying the composition of the precursor feedstock, a composition gradient coating
3 can be formed having nanoparticle size particles of less than 100 nm. Many combinations of
4 materials can be co-deposited, such as ceramics-ceramics, metal-ceramics, metal-metal, and organic-
5 inorganic. By applying an external energy source either during the coating process or during post
6 deposition, the resulting coating can be modified.

7 A further feature of the invention is that multifunctional, multilayered, nanostructured
8 coatings can be better prepared by using solution feedstocks in the thermal spray deposition process.
9 This permits tailored engineering of the interfaces at a finer length scale by compositional and
10 microstructural grading throughout the entire coating thickness. This process permits an efficient
11 conversion of molecules-atoms (solution dependent) into aerosol droplets and subsequent chemical
12 reactions to form the product layers on the substrate. With post-deposition treatment of the as-
13 synthesized coating, there can be optimized microstructures, structures, density and adhesion.

14 By using thermal spraying of solution precursor feedstocks, compositionally and
15 microstructurally graded coatings are fabricated which have unique advantages. The molecular level
16 mixing of the constituents in solution precursor feedstocks allows for better chemical homogeneity
17 of sprayed products. By using fine droplets that are many times smaller than the conventionally used
18 powder feedstock (e.g. 30 microns or larger in particle size), a finer scale of microstructure can be
19 achieved. The solidification of droplets can be controlled in flight or on impact on the substrate by
20 controlling the spray temperature, the working distance and the substrate temperature. This provides

Inventor's Name: Gan-Moog Chow, Lynn K. Kurihara, T. Danny Xiao, Peter R. Strutt,
Christopher W. Strock and Raymond A. Zatorski

1 a means to reduce the size of microstructure as compared to the powder feedstock routes. Finally,
2 functional grading of multilayered coatings can be achieved at a much finer scale, particularly for
3 nanostructured graded coatings, both compositionally and microstructurally, compared to the powder
4 feedstock approach wherein the size of splat poses a limit on the scale of mixing and grading.
5 Functional grading may include, but is not limited to, the graded continuous interface where the
6 microstructure, structure and chemistry of two or more materials are varied continuously. Such
7 grading may enhance the thermal, chemical and mechanical stability of multilayerd coatings and the
8 control of the mechanical, electrical, magnetic and other transport properties.

9

10 **Brief Description of the Drawings**

11 Fig. 1 illustrates a schematic diagram for the coating process.

12 Fig. 2 illustrates a gradient coating in the form of a graph showing the relative concentrations
13 of the two components A and B as a function of the distance from the substrate S.

14

15 **Description of the Preferred Embodiments**

16 As shown schematically in Fig. 1, a thermal spray coating apparatus such as the Metco 9MB-
17 plasma torch can be fitted with a GH nozzle, and the powder injection port is removed and replaced
18 with multiple injection nozzles which are incorporated and arranged with para-axial or oblique angle
19 injection into the plasma flame. As seen in Fig. 1, the thermal spray gun 10 has a flame generating
20 tube 12 from which the flame 13 extends. Adjacent the flame is the liquid supply chamber 14 which

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1 will direct the liquid into the flame. The multiple injection nozzles 16 in the chamber 14 permit
2 controlled and varying amounts of the various component feedstock solutions to be applied to the
3 plasma spray gun. The coating mixture is then sent through the flame and onto the substrate 18. This
4 setup can be mounted on a 6-axis GM-Fanue robot. A high-pressure chemical metering pump can
5 be used to feed the solutions to the nozzles. Preferably, the primary and secondary arc gases are
6 argon and hydrogen respectively, and the atomization gas is nitrogen.

7 Deposition of ceramic coatings using solution feedstocks can be made with coatings greater
8 than or equal to 40 microns thick of alumina, zirconia, yttria stabilized zirconia, as well as
9 compositionally graded alumina-zirconia-alumina and graded alumina-yttria stabilized zirconia on
10 stainless steel substrates. The feedstocks include aqueous solution of aluminum nitrate, alcohol-
11 water solution of aluminum tri-sec butoxide, alcohol-water solution of zirconium n-propoxide, and
12 alcohol-water solution of yttrium nitrate and zirconium n-propoxide. Thinner coatings can also be
13 made by running a fewer number of thermal spray passes over the substrate. The solution precursors
14 may include organometallic, polymeric, and inorganic salts materials, which should be cost efficient
15 for a particular deposition. Preferred inorganic salts are nitrates, chlorides and acetates.

16 Adherent and smooth coatings can be prepared, depending on the specific deposition
17 conditions such as spray working distance. Characterization of coatings' structure, microstructure,
18 and adhesion included analysis by x-ray diffraction, scanning electron microscopy and energy
19 dispersive spectroscopy.

20 Post deposition techniques may include conventional furnace heat treatment, UV lamp, laser,

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1 microwave, and other beam sources at various wavelengths. The post deposition techniques may also
2 be employed simultaneously, or in sequence, during cycles of thermal spraying of the liquid
3 precursors, so as to control the microstructure, structure, chemistry and interfaces properties, and
4 porosity etc.

5 Fig. 2 illustrates a substrate, S, on the left to which a coating of components A and B have
6 been added as a gradient coating. The two curved lines indicate the % of each component in the total
7 coating at each height above the substrate. Initially, at the substrate surface, the only coating
8 component is A and the amount of B is zero. Then as the spray coating continues to build up the
9 coating, more of B is added until, when the height in region 2 is reached, the concentration of each
10 component is about the same. This trend of increasing the relative amount of B continues until at
11 region 3, the composition is all B. Finally, the third coating layer is built by increasing the A
12 component until it is all A in region 5.

*JNS
A12*
~~Fig. 2 illustrates how the gradient can be finely controlled to change from one composition to another by using the solution precursors. The three component layer shown in Fig. 2 also illustrates how the three layers can be built up with good adherence between the layers due to the gradient transition between them. When coating A is alumina, it provides good adherence to the substrate. When coating B is zirconia, it provides thermal resistance properties. By applying a second layer of A of alumina, it provides oxygen protection to the intermediate zirconia layer. Such a concept of graded coatings can be used in other applications as well and by using other materials.~~

20 As seen in Fig. 1, the thermal spray apparatus can have a series of injection nozzles in the

1 spray gun mechanism to deliver the various combination of liquid coating components. Alternative
2 spraying devices could be used in which two spray guns could be positioned side by side to deliver
3 two separate compositions, or other combinations of multiple guns can be used.

4 In another embodiment, it is possible to add small pre-formed particles to the liquid feedstock
5 solution as suspended particles. When co-spraying the suspended particles together with the same
6 liquid carrier, it is preferred to add a surfactant which allows the nanostructured particles to be
7 somewhat agglomerated to only a few microns, but definitely smaller than the conventional 30 or
8 larger micron agglomerate size. This embodiment is useful when applying materials that are not
9 stable in the liquid state, or when applying two components A and B where they would be
10 undesirably reactive in the liquid state while they were being applied.

11 By using the process of this invention, the coating artisan is given the capability of making
12 thin or thick coatings which are made of nanostructured particles which have a diameter of less than
13 about 100 nm (0.1 micron). Each layer can be as thin as about 100 nm, but the particle size (or
14 crystallite size) in each layer must be less than 100 nm.

15 Conventional thermal spraying of thick coating will only give particles of at least several
16 microns in one dimension , i.e. the thickness of the splat. Even electroplating is not a straight
17 forward procedure for grading, since the conductivities of different species vary normally, and thus
18 result in non-stoichiometric deposition.

19 Examples

20 Having described the basic aspects of the invention, the following examples are given to

1 illustrate specific embodiments thereof.

Example 1

3 This example illustrates the production of a multilayer coating according to the present
4 invention.

The following solutions were used as the feedstocks: 0.5 M aluminum nitrate (AN); 0.5 M aluminum tri-sec- butoxide (ASB); 0.5 M zirconium n-propoxide; and 0.5 M zirconium n-propoxide with 4 wt% yttria. The alkoxide solutions were made by dissolving the alkoxide in an ethanol-acetic acid solution and then adding water. The aluminum nitrate solution was prepared by dissolving the appropriate amount of the salt in distilled deionized water. The nitrate has the advantage of being very inexpensive, and there are no undesirable secondary reactions. However, the nitrate has been suggested to interfere with the stabilization of zirconia, and if large amounts of solution are used the NO_x ($x=1, 2$) from the decomposition of the nitrate may be a problem. The alkoxide, on the other hand, is more expensive as compared to the nitrate (but the amount of alumina is not the major component) and the alkoxide is reactive with water. It has been shown to stabilize zirconia at 10%.

15 The graded sample was prepared by spraying 20 passes of the aluminum nitrate solution,
16 stopping and then running distilled water through the line to remove the AN solution. This was
17 sprayed into a bucket and not on the substrate. Then, the solution was changed to zirconia
18 (unstabilized) and sprayed until the ZrO₂ sol had replaced the water. Then, the plasma was started
19 and the 20 passes were sprayed on the substrate. Again, the system was flushed with water and the
20 AN sol was used again. The result was a graded coating of alumina-zirconia-alumina on a steel

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1 substrate as characterized by Run 1a in Table 1. The crystallite size was obtained by x-ray line
 2 broadening, and the microstructure by scanning electron microscopy. The chemistry was
 3 characterized by energy dispersive x-ray spectroscopy.

4 Table 1

5 Run	6 Solution feedstock	7 Phase of deposited 8 coatings	9 Average crystallite 10 size (nm)
11 1a	Graded AN-ZP-AN	monoclinic ZrO_2	19
		tetragonal ZrO_2	25
		alpha alumina	37
12 1b	aluminum nitrate (AN)	gamma alumina	14
13 1c	aluminum sec-butoxide (ASB)	gamma alumina	67
14 1d	yttria stabilized Zr n-propoxide (ZP)	tetragonal ZrO_2	42

15 For Run 1a, the two alumina layers had an average crystallite size of 37 nm. For the
 16 intermediate zirconia layer, there were two phases present.

17 Additional runs were made with three solutions as set forth in Runs 1b-1d in Table 1. All of
 18 the average crystallite sizes were less than 80 nm. The data shows that nanostructured coatings were
 fabricated.

19 The difference in the nature of the alumina layer in Runs 1a and 1b is due to the existence
 20 of Zr which acts as a thermal barrier. Most of the heat is trapped in the Zr layer, and so it allows a
 21 higher temperature phase of alumina to be formed in Run 1a. In Run 1b, most of the heat is

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1 conducted away to the substrate so that a low temperature phase of alumina is formed.

2 Example 2

3 A systematic investigation of coating parameters was carried out. All solutions were prepared
4 from aluminum nitrate at the molar concentration given in Table 2. Samples were characterized by
5 XRD if the coating adhered to the substrate.

6 In the following Table 2, the relative plasma temperature was determined by measuring by
7 the current in amperes divided by the gas flow in standard cubic feet per hour. The aluminum nitrate
8 concentration is measured in moles/liter and the speed is in mm/sec. The spray distance is in inches
9 and the term "OOR" indicates that the grain size was "out of range" meaning that it was larger than
10 100 nm.

11 Table 2

13 Sample	14 Plasma	15 particle	16 concen-	17 speed	18 spray	19 Grain	20 phase	21 Adhere
No.	Temp	size	tration		distance	Size		
1a	6.875	0	0.5	20	1.5	17	gamma	Y
1b	6.875	0	0.5	20	2	97	gamma	Y
1c	6.875	0	0.5	20	2.5	OOR	gamma	Y
1d	6.875	0	0.5	20	3			N
2a	6.875	0	1.25	1000	1.5			N
2b	6.875	0	1.25	1000	2			N
2c	6.875	0	1.25	1000	2.5			N

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1	2d	6.875	0	1.25	1000	3			N
2	3a	6.875	35	0.5	1000	1.5			N
3	3b	6.875	35	0.5	1000	2			N
4	3c	6.875	35	0.5	1000	2.5			N
5	3d	6.875	35	0.5	1000	3			N
6	4a	6.875	35	1.25	20	1.5			N
7	4b	6.875	35	1.25	20	2			N
8	4c	6.875	35	1.25	20	2.5			N
9	4d	6.875	35	1.25	20	3			N
10	5a	8.125	0	0.5	1000	1.5	29	Gamma	Y
11	5b	8.125	0	0.5	1000	2			N
12	5c	8.125	0	0.5	1000	2.5			N
13	5d	8.125	0	0.5	1000	3			N
14	6a	8.125	0	1.25	20	1.5	OOR	alpha	Y
15	6b	8.125	0	1.25	20	2	135	alpha	Y
							18	gamma	
16	6c	8.125	0	1.25	20	2.5	15	gamma	Y
17	6d	8.125	0	1.25	20	3	37	gamma	Y
18	7a	8.125	35	0.5	20	1.5	28	gamma	Y
19	7b	8.125	35	0.5	20	2			N
20	7c	8.125	35	0.5	20	2.5	30	gamma	Y
21	7d	8.125	35	0.5	20	3	30	gamma	Y
22	8a	8.125	35	1.25	1000	1.5			N
23	8b	8.125	35	1.25	1000	2	38	gamma	Y
24	8c	8.125	35	1.25	1000	2.5			N
25	8d	8.125	35	1.25	1000	3	37	gamma	Y
26									

27 Qualitative observations can be made from the data in Table 2. First, the adhesion of the

1 liquid coating is generally better than when spraying the particles themselves because the particles
2 did not have enough thermal energy to form a true bonding with the substrate or with themselves
3 under the same conditions as the liquid spray. Second, the table demonstrates the need for careful
4 control of parameters to optimize the coating.

5

6 Example 3

7 Investigation of grading composition was carried out using six premixed solutions of
8 aluminum sec butoxide (ASB) and zirconium n-propoxide (ZP), using volume ratios of a total
9 volume of 100 mL as set forth in Table 3.

10 Table 3

Coating	ASB %	ZP %
1	100	0
2	90	10
3	70	30
4	50	50
5	30	70
6	10	90

20 The deposition time (t) (as measured by the time the solution was passed through the gun)
21 and the working distance (D) between the gun and substrate were investigated and the results are set
22 forth in Table 4.

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Table 4

Run No.	Time & distance	Phase(s) detected Major phase listed first	Average Crystallite Size (nm)
1	t: 1 min D: 1"	Tetragonal ZrO ₂	12
		Monoclinic ZrO ₂	8
		alumina	2
2	t: 1 min D: 2"	Tetragonal ZrO ₂	21
		Monoclinic ZrO ₂	17
		alumina	15
3	t: 1.5 min D: 1"	Tetragonal ZrO ₂	20
		Monoclinic ZrO ₂	19
		alumina	43
4	t: 1.5 min D: 2"	Tetragonal ZrO ₂	10
		alumina	4
5	t: 2 min D: 1"	Monoclinic ZrO ₂	58
		Tetragonal ZrO ₂	59
		alumina	13
6	t: 2 min D: 1.5"	Tetragonal ZrO ₂	17
		Monoclinic ZrO ₂	14
		alumina	45
7	t: 2 min D: 2"	Tetragonal ZrO ₂	11
		alumina	11

10

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1 The alumina phase matches JCPDS card 37-1462 (from coprecipitated mixture at 500°C).

2 This may suggest that nucleation of low temperature alumina phase at the surface of substrate, which
3 is different form the high temperature deposition of molten alumina particles in conventional thermal
4 spraying.

5 It is understood that the foregoing detailed description is given merely by way of illustration
6 and that many variations may be made therein without departing from the spirit of this invention.

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100